

Equation of State of Alkane and Alkylbenzene Liquids: A Test of the Group Contributions of Scaling Parameters for Physical and Chemical Mixtures

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The equation of state (EOS) data for physical and chemical mixtures have been studied in terms of the Simha–Somcynsky hole theory. In a previous paper, individual group attraction energy and repulsive volume quantities necessary for the description of interactions between the chemical constituents of alkanes and alkylbenzene were proposed. The previous method has now been extended to physical mixtures of alkanes and alkane–alkylbenzene through suitable decomposition equations for physical and chemical mixtures. A comparison of the theoretical EOS data, predicted by means of the proposed scaling parameters, and the experimental data is in reasonable agreement. The results confirm a basis for the EOS predictions and promote applications of the methodology to further systems.

KEY WORDS: alkanes; alkylbenzene; equation of state; mixtures; Simha–Somcynsky theory.

1. INTRODUCTION

The thermodynamics of fluids with dense chain molecules is an important subject from the point of view of both their physical specifications and a generalization of statistical thermodynamics of simple fluids. In our treatise, the cell model of Lennard–Jones and Devonshire [1], generalized to assemblies of chain molecules due to Prigogine et al. [2, 3], is employed. Simha and Somcynsky (SS) [4] made an arrangement in the model increasing the disorder by utilizing vacancies or holes in the underlying

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quasi-lattice. An established equation of state was intensively applied to low- and high-molar mass fluids [5], with significant quantitative achievement. It was extended to related mixtures [6]. In this manner, characteristic scaling parameters have been obtained for a large number of polymers [7, 8]. In recent years, some modification in the theory have been proposed to get better results [9].

The purpose here is not to establish the theory's performance. However, the quantitative success of the hole theory encouraged us to engage in a detailed structural analysis. In the earlier work, our concern was to arrive at generalizing principles, chemically based on molecular structure. From the results of structure analysis, chemical group characteristic parameters were extracted [10, 11].

In this context, the applicability of the extracted parameters for some physical mixtures as well as chemical mixtures is explored. Our present concern is oligomeric hydrocarbon mixtures, in the lubricating range of molar mass and to predict their equation of state (EOS) data. For these fluids, we have established the decomposition equations for both physical and chemical mixtures.

2. PRELIMINARIES

In our treatise, the cell model of Lennard-Jones and Devonshire [1] generalized to assemblies of chain molecules due to Prigogine et al. [2, 3] is employed. In the cell theory, the reference unit, molecule or segment, is allowed to move and is subject to molecular interaction with its neighbors, determined by a specified pair potential. In 1969, Simha and Somcynsky (SS) [4] made an arrangement in the model increasing the disorder by employing holes in the quasi-lattice. The temperature- and volume-dependent occupied site fraction, $y(V, T)$, is assumed to be for an M multicomponent system

$$y = \frac{\sum_{i=1}^M s_i N_i}{\sum_{i=1}^M s_i N_i + N_h} \quad (1)$$

where N_i ($1 < i < M$) is the number of i th component molecules, N_h is the number of holes, and s_i is the number of segments for the i th molecule. The configurational partition function for the N_i ($1 < i < M$) molecular system is given by [6, 12]

$$Z_{\text{conf}} = g(N, y)[v_f(V, y)]^{\sum_i c_i N_i} \exp[-E_0(V, T, y)/kT] \quad (2)$$

The first factor in Eq. (2) is the combinatorial factor for mixing of occupied and unoccupied sites and is given by

$$g(N, y) \propto y^{-N}(1-y)^{-\sum_i s_i N_i (1-y)/y} \quad (3)$$

where $N = \sum_i N_i$. The second factor in Eq. (2) represents the free volume quantity, given by linearly length-averaged solid-like and gas-like contributions weighted by the occupied and unoccupied fractions, respectively, as [4]

$$v_f = \langle v^* \rangle \{ y[(y\tilde{V})^{1/3} - 2^{-1/6}] + (1-y)(y\tilde{V})^{1/3} \}^3 \quad (4)$$

where the smoothed cell potential model is employed for the former [2, 3]. The exponent $3c_i$ in the second factor is the number of external degrees of freedom of the i th molecule. The last exponential factor is the total lattice energy with the assumed Lennard-Jones-type pair potential for N molecules,

$$2E_0 = yN \langle qz \rangle \langle \phi \rangle \quad (5)$$

$$\langle \phi \rangle = \langle \varepsilon^* \rangle [1.011(v^*/\omega)^4 - 2.409(v^*/\omega)^2]$$

with $\omega = yv$ and $\langle qz \rangle = \langle s \rangle (\langle z \rangle - 2) + 2$ the number of interchain nearest-neighbors in the lattice of coordination number $z = 12$. $\langle v^* \rangle$ and $\langle \varepsilon^* \rangle$ are the average characteristic repulsive volume and attractive energy corresponding to the potential minimum at r^* . We decompose these parameters into constituents in the next section. The EOS is formulated in terms of the reduced volume, temperature, and pressure, *viz.*,

$$\tilde{V} = V/V^*, \quad \tilde{T} = T/T^*, \quad \tilde{P} = P/P^* \quad (6)$$

where the scaling parameters are as follows: V^* is defined by the molar volume $\langle s \rangle \langle v^* \rangle$, T^* by $\langle qz \rangle \langle \varepsilon^* \rangle / \langle c \rangle k$ as a balance between the attraction and the thermal energy contributed by the external degrees of freedom, and P^* is defined by the ratio between the chain attraction energy $\langle qz \rangle \langle \varepsilon^* \rangle$ and the volume $\langle s \rangle \langle v^* \rangle$. From these definitions, there follows

$$(P^*V^*/T^*) \langle M_0 \rangle = (\langle c \rangle / \langle s \rangle) R \quad (7)$$

where

$$\langle c \rangle = \sum_i x_i c_i \quad (8)$$

$$\langle s \rangle = \sum_i x_i s_i \quad (9)$$

and

$$\langle M_o \rangle = \sum_i s_i x_i M_{oi} / \langle s \rangle \quad (10)$$

with M_{oi} the segmental mass of the i th molecule.

The EOS of SS yields the following equation, derived from the configurational Helmholtz energy, A , and the thermodynamic relations

$$P = -(\partial A / \partial V)_{T, N} \quad (11)$$

$$\tilde{P}\tilde{V} / \tilde{T} = (1 - Q)^{-1} + (2y / \tilde{T})(y\tilde{V})^{-2} [1.011(y\tilde{V})^{-2} - 1.2045]$$

where $Q = 2^{1/6}y(y\tilde{V})^{-1/3}$. The occupied site fraction, $y(V, T)$ can be obtained by minimization of the Helmholtz energy of an ensemble,

$$(\partial F / \partial y)_{V, T, \langle c \rangle / \langle s \rangle} = 0$$

$$(\langle s \rangle / 3 \langle c \rangle) [(\langle s \rangle - 1) / \langle s \rangle + y^{-1} \ln(1 - y)]$$

$$= (y / 6\tilde{T})(y\tilde{V})^{-2} [2.409 - 3.033(y\tilde{V})^{-2}] + (Q - 1/3)(1 - Q)^{-1} \quad (12)$$

The resultant EOS was extensively applied to low- and high-molar mass fluids. In this manner, characteristic scaling parameters have been obtained for a large number of polymers [8].

3. THEORY

3.1. Mixtures of Alkanes

The equation of decomposition for a single-component fluid with a chemically multiconstituent molecular system has been investigated recently by several authors [10, 11]. Here we extend the work to the multicomponent fluid as well. Let us consider M different-length paraffins, with the $n_i - 2$ internal and two terminal units denoted a and b , respectively, for the i th molecule. The pertinent interaction energy and repulsive volume parameters, ε_{kl}^* and v_{kl}^* ($k, l = a, b$), defined for a single-component fluid, are assumed to be the same for the multicomponent one. These parameters are related with the average interaction and repulsive volume parameters, $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$, respectively. The intermolecular contact numbers for the internal (a) and terminal (b) units for the i th molecule are

$$q_{ia}z = (n_i - 2)(z - 2) \quad \text{and} \quad q_{ib}z = 2(z - 1) \quad (13)$$

with the corresponding contact probabilities

$$P_a = \frac{\sum_{i=1}^M x_i q_{ia} z}{\sum_{i=1}^M x_i q_i z} = \frac{\langle q_a z \rangle}{\langle q z \rangle} \quad (14)$$

$$P_b = 1 - P_a = \frac{\sum_{i=1}^M x_i q_{ib} z}{\sum_{i=1}^M x_i q_i z} = \frac{\langle q_b z \rangle}{\langle q z \rangle} \quad (15)$$

with the component fraction $x_i = N_i / \sum N_i$ and the contact number of pairs $q_i = q_{ia} + q_{ib} = n_i(z-2) + 2$ for the i th molecule.

Defining the interaction function ϕ_{kl} in analogy with Eq. (5),

$$\phi_{kl} = \varepsilon_{kl}^* \{1.011(v_{kl}^*/\omega)^4 - 2.409(v_{kl}^*/\omega)^2\}, \quad k, l = a, b \quad (16)$$

with $\omega = yv$, the lattice energy equals

$$2E_0 = yN[\langle q_a z \rangle (P_a \phi_{aa} + P_b \phi_{ab}) + \langle q_b z \rangle (P_a \phi_{ab} + P_b \phi_{bb})] \quad (17)$$

Upon writing the same quantity in terms of averages $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$ in accordance with Eq. (5), and identifying coefficients of ω^{-4} and ω^{-2} , the following two sets of equations ensue, with $m=2, 4$:

$$\langle q z \rangle^2 \langle \varepsilon^* \rangle \langle v^* \rangle^m = \langle q_a z \rangle^2 \varepsilon_{aa}^* v_{aa}^{*m} + \langle q_b z \rangle^2 \varepsilon_{bb}^* v_{bb}^{*m} + 2 \langle q_a z \rangle \langle q_b z \rangle \varepsilon_{ab}^* v_{ab}^{*m} \quad (18)$$

3.2. Mixtures of Linear and Ringed Alkanes

In this section, we analyze the contributions of interaction parameters of M different structures as both alkanes and alkanes with a ring attachment. In the analysis of an n -mer, the segments into which the molecule was decomposed were identified with the chemical repeat unit and placed on the lattice sites. This is no longer the case for rings, and a single site is used to accommodate one unit, so that the comparatively large ring is decomposed into s_r units. The determination and values of the s_r segments for some rings have been discussed elsewhere and are shortly discussed below. The actual and symbolized structures are depicted in Ref. 11.

In addition to the contact numbers of linear chain molecules as in Eq. (13), those of an alkyl with a segment length s_i for $s_i - 1$ internal a and one terminal b , and a ring with s_r ring units are given, respectively, by

$$q_{ia} z = (s_i - s_r - 1)(z - 2), \quad q_{ib} z = z - 1, \quad q_{ir} z = s_r(z - 2) + 1 \quad (19)$$

where $q_i z = q_{ia} z + q_{ib} z + q_{ir} z$. The corresponding contact probabilities of the mixtures of alkanes and alkanes with a ring are

$$P_a = \frac{\langle q_a z \rangle}{\langle q z \rangle}, \quad P_b = \frac{\langle q_b z \rangle}{\langle q z \rangle}, \quad P_r = 1 - P_a - P_b = \frac{\langle q_r z \rangle}{\langle q z \rangle} \quad (20)$$

where $\langle q z \rangle = \sum_{i=1}^M x_i q_i z$ and $\langle q_k z \rangle = \sum_{i=1}^M x_{ik} q_{ik} z$, with $k = a, b$, and r .

Defining the interaction ϕ_{kl} ($k, l = a, b$, and r) by analogy with Eq. (16), the lattice energy can be cast as

$$2E_0 = yN[\langle q_a z \rangle (P_a \phi_{aa} + P_b \phi_{ab} + P_r \phi_{ar}) + \langle q_b z \rangle (P_a \phi_{ab} + P_b \phi_{bb} + P_r \phi_{br}) + \langle q_r z \rangle (P_a \phi_{ar} + P_b \phi_{br} + P_r \phi_{rr})] \quad (21)$$

Comparing the same quantity in terms of averages $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$ according to Eq. (5), the following two sets of equations give

$$\begin{aligned} \langle q z \rangle^2 \langle \varepsilon^* \rangle \langle v^* \rangle^m &= \langle q_a z \rangle^2 \varepsilon_{aa}^* v_{aa}^{*m} + \langle q_b z \rangle^2 \varepsilon_{bb}^* v_{bb}^{*m} + \langle q_r z \rangle^2 \varepsilon_{rr}^* v_{rr}^{*m} \\ &+ 2\langle q_a z \rangle \langle q_b z \rangle \varepsilon_{ab}^* v_{ab}^{*m} + 2\langle q_a z \rangle \langle q_r z \rangle \varepsilon_{ar}^* v_{ar}^{*m} \\ &+ 2\langle q_b z \rangle \langle q_r z \rangle \varepsilon_{br}^* v_{br}^{*m} \end{aligned} \quad (22)$$

with $m = 2$ and 4.

4. NUMERICAL ANALYSIS

4.1. *n*-Alkane Mixtures

About half a decade ago, Simha and Yahsi [11] decomposed the segmental parameters of the linear paraffins into their constituents using the API (American Petroleum Institute) Project data due to Schiessler and co-workers [13, 14]. In this work, they utilized linear chain molecules from chain length $n = 12$ through $n = 32$. The characteristic parameters P^* , V^* , T^* , and c had been calculated using the broad range of temperature (273 to 408 K) and pressure data (up to 344.5 MPa), and then $\langle v^* \rangle$ and $\langle \varepsilon^* \rangle$ were determined by the definition of the scaling parameters in Eq. (6). The best-fit c equation as a measure of the degrees of freedom was obtained as

$$c = (n-2) c_i + 2c_e \quad (23)$$

with $c_i = 0.070$ and $c_e = 0.5815$. We note that the use of Eq. (23) in the theory gives satisfactory performance [11] and is considered to be valid for the physical mixtures with the aid of Eq. (8). The characteristic parameters,

$\langle v^* \rangle$ and $\langle \varepsilon^* \rangle$, were decomposed into group contributions, v_{kl}^* and ε_{kl}^* , for the constituents of a molecule. (See Ref. 11 for the values.) Assuming that these parameters are valid for physical mixtures as well, we calculate the necessary characteristic parameters, $\langle v^* \rangle$ and $\langle \varepsilon^* \rangle$, for physical mixtures, reading Eq. (18) from right to left, and then P^* , T^* , and V^* from Eqs. (6) and (7) necessary for the theoretical scaling.

The experimental information is taken from Kanti [15], Zhou et al. [10], and Dymond et al. [16]. The scaling parameters outlined above are listed in Tables I and II for the paraffin mixtures. All the parameters are average values with respect to their respective fractions and their constituent group contributions. These parameters are then tested using theory to predict the volumetric data with respect to all the given pressures and temperatures. Tables I and II summarize the results of the computations in terms of the mean and maximum volumetric percentage errors. The measurements of the mean and maximum deviations in volume between theory and experiment are defined by

$$N\Delta V_{\text{mean}} = \sum \Delta V_i \quad (24)$$

$$\Delta V_{\text{max}} = \text{Max}(\Delta V_i)$$

where $\Delta V_i = 100 |V_{i, \text{th}} - V_{i, \text{exp}}| / V_{i, \text{exp}}$ and N is the number of data.

The experimental data for mixtures of C_{10} and C_{14} paraffins are listed for n -heptane weight fractions of 0, 0.15, 0.25, 0.35, 0.50, 0.60, 0.75, 0.90, and 1.0 with their respective molar fractions in Table I. These data are given

Table I. Characteristic Average Parameters for $x C_{10}H_{22} + (1-x) C_{14}H_{30}$ Mixtures

	x								
	0.0	0.197	0.317	0.429	0.582	0.677	0.807	0.926	1.00
$10^{-6}\langle v^* \rangle$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	17.579	17.652	17.701	17.751	17.825	17.874	17.949	18.024	18.074
$\langle \varepsilon^* \rangle$ (K)	154.99	155.90	156.50	157.10	157.98	158.55	159.41	160.26	160.82
$10^{-3}\langle V^* \rangle$ ($\text{m}^3 \cdot \text{kg}^{-1}$)	1.2406	1.2450	1.2480	1.2509	1.2554	1.2584	1.2628	1.2673	1.2703
$\langle T^* \rangle$ (K)	10988	10734	10572	10416	10192	10049	9842.6	9646.3	9520.6
$\langle P^* \rangle$ (MPa)	743.5	745.4	746.7	747.8	749.5	750.6	752.2	753.7	754.6
ΔV_{mean} (%)	0.11 (0.10)	0.17 (0.14)	0.17 (0.15)	0.19 (0.18)	0.21 (0.30)	0.26 (0.29)	0.28 (0.32)	0.35 (0.43)	0.33 (0.41)
ΔV_{max} (%)	0.18 (0.18)	0.26 (0.27)	0.26 (0.27)	0.49 (0.49)	0.43 (0.67)	0.50 (0.50)	0.53 (0.53)	0.83 (0.97)	0.64 (0.69)

Table II. Characteristic Average Parameters for Some Paraffin Mixtures

	$x\text{C}_6 + (1-x)\text{C}_{16}$ ($x = 0.4$)	$x\text{C}_{10} + (1-x)\text{C}_{16}$ ($x = 0.5$)	$x[\text{C}_{14} + \text{C}_{16}] + (1-2x)\text{C}_{10}$ ($x = 0.2$)
$10^{-6}\langle v^* \rangle$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	17.784	17.673	17.784
$\langle \varepsilon^* \rangle$ (K)	157.50	156.16	157.50
$10^{-3}\langle V^* \rangle$ ($\text{m}^3 \cdot \text{kg}^{-1}$)	1.2530	1.2462	1.2529
$\langle T^* \rangle$ (K)	10313	10664	10313
$\langle P^* \rangle$ (MPa)	748.6	746.0	748.6
ΔV_{mean} (%)	0.47	0.37	0.42
ΔV_{max} (%)	0.75	0.55	0.70

for the temperature range 313 to 353 K up to 40 MPa (up to 100 MPa by the Tait equation [15]). The percentage mean error in volume ranges from 0.11 (0.10) to 0.35 (0.43) up to 40 MPa (up to 100 MPa in parentheses). One observes the increasing deviation if one goes from C_{14} to C_{10} , because the decomposed parameters in Ref. 11 are obtained for chain lengths from $n = 12$ through $n = 32$. Below chain length 12, the parameters are extrapolated. Even using the chain length $n = 10$ paraffin, we ended up with a reasonable performance in the theory. This shows how the decomposed parameters are working for the alkane mixtures as well as for the pure alkanes, even though the chain length is out of the range obtained.

The same is almost true for different kinds of mixtures in Table II. Mean and maximum errors in binary 0.4C_6 and 0.6C_{16} , binary 0.5C_{10} and 0.5C_{16} , and ternary $0.2(\text{C}_{14} + \text{C}_{16})$ and 0.6C_{10} paraffin mixtures are 0.47 and 0.75, 0.37 and 0.55, and 0.42 and 0.70, respectively. Considering the different sets and sources of experimental information, the consistency and applicability of the group contribution of the characteristic parameters seem to be reasonable.

4.2. Mixtures of Alkanes and Alkylbenzene

In this section, to verify the importance of the group contributions due to the different units in the chain molecules in binary and ternary mixtures, we analyze the contributions of mixtures of alkanes and alkylbenzene. The analysis is guided by the results for n -alkanes discussed above. There the segments that the molecule was decomposed into were identified with the chemical repeat unit and placed on the lattice sites. In this case, the size disparities between different groups are sufficiently small to be neglected. In the case of rings, this is no longer the case, and the ring must be decomposed into subunits. Simha and Yahsi defined a quasi-segment for

ring structure, so that it corresponds to the same segmental volume as in the corresponding normal alkane. This was based on a principle of corresponding states employed by Hijmans [17] for n -alkanes from a phenomenological perspective, to define segments of an n -mer. This requires shifts of the V - T curves. A corresponding segment evaluated for benzene rings gives $s_b = 4.7$ [11]. Owing to the decomposition of the ring, alkyl benzene is treated as an s -mer: n alkyl plus an s_b ring segment. For the dependence of the c parameter on the chain length in the equivalent chain model, we make use of Eq. (23) in terms of s substituted for n .

The group contributions involving the benzene-equivalent ring segment, v_{kr}^* and ε_{kr}^* , ($k = a, b$, or r , and r refers to the benzene segment) for the constituents of the benzene ring are given in Ref. 11. Assuming these parameters to be valid for physical mixtures as well, we calculate the necessary characteristic parameters $\langle v^* \rangle$ and $\langle \varepsilon^* \rangle$ for a given mixture, reading Eq. (22) from right to left, and then P^* , T^* , and V^* as necessary for the theoretical scaling.

The density data are given from atmospheric to 40 MPa pressure and extrapolated with the Tait equation up to 100 MPa in the temperature range 313 to 353 K in the thesis of Kanti [15]. All the parameters outlined above for the mixtures are listed in Tables III–V and are the average values with respect to their respective molar fractions and their constituent group contributions. These parameters are then tested by theoretically predicted volumetric data with respect to all the given pressures and temperatures. The tables summarize the results of the computation in terms of volumetric percentage error in mean and maximum.

Table III. Characteristic Average Parameters for x n -Butylbenzene + $(1-x)$ C_{14} Mixtures

	x								
	0.00	0.207	0.330	0.443	0.596	0.689	0.816	0.930	1.00
$10^{-6}\langle v^* \rangle$ ($m^3 \cdot mol^{-1}$)	17.579	17.490	17.426	17.358	17.248	17.169	17.038	16.892	16.784
$\langle \varepsilon^* \rangle$ (K)	154.99	158.25	160.27	162.15	164.74	166.29	168.35	170.11	171.11
$10^{-3}\langle V^* \rangle$ ($m^3 \cdot kg^{-1}$)	1.2406	1.2192	1.2047	1.1901	1.1677	1.1524	1.1289	1.1047	1.0880
$\langle T^* \rangle$ (K)	10988	10765	10611	10452	10206	10038	9778	9512	9331
$\langle P^* \rangle$ (MPa)	743.5	764.0	777.2	790.0	808.8	820.9	838.5	855.8	867.1
ΔV_{mean} (%)	0.11 (0.10)	0.26 (0.36)	0.22 (0.31)	0.23 (0.29)	0.42 (0.48)	0.60 (0.67)	0.55 (0.55)	0.94 (0.94)	1.20 (1.17)
ΔV_{max} (%)	0.18 (0.18)	0.50 (0.71)	0.43 (0.48)	0.46 (0.55)	0.66 (0.66)	0.84 (0.94)	0.80 (0.80)	1.16 (1.16)	1.43 (1.43)

Table IV. Characteristic Average Parameters for $x\text{C}_7$ Mixtures + $(1-x)$ n -Nonylbenzene

	x								
	0.0	0.097	0.265	0.405	0.523	0.671	0.754	0.860	1.00
$10^{-6}\langle v^* \rangle$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	16.749	16.842	17.036	17.239	17.448	17.771	17.987	18.307	18.817
$\langle \varepsilon^* \rangle$ (K)	166.41	165.94	165.13	164.55	164.22	164.23	164.58	165.64	168.78
$10^{-3}\langle V^* \rangle$ ($\text{m}^3 \cdot \text{kg}^{-1}$)	1.1229	1.1315	1.1494	1.1680	1.1870	1.2165	1.2364	1.2661	1.3146
$\langle T^* \rangle$ (K)	11671	11354	10778	10272	9830	9263	8943	8539	8032
$\langle P^* \rangle$ (MPa)	838.2	831.8	819.5	808.1	797.9	785.1	778.4	771.2	767.1
ΔV_{mean} (%)	0.21 (0.31)	0.15 (0.21)	0.20 (0.22)	0.37 (0.49)	0.63 (0.70)	0.76 (0.90)	0.84 (0.97)	0.88 (1.06)	0.60 (1.00)
ΔV_{max} (%)	0.39 (0.47)	0.25 (0.32)	0.40 (0.42)	0.60 (1.00)	0.90 (0.93)	1.10 (1.26)	1.22 (1.30)	1.34 (1.42)	1.11 (1.68)

Mixtures of samples are characterized by the molar fraction κ and shown in the tables in molar fractions, but they are measured in weight fractions in Kanti's thesis [15]. In Table III, butylbenzene and n -tetradecane binary mixtures have been measured with the butylbenzene molar fractions of 0, 0.207, 0.330, 0.443, 0.596, 0.689, 0.816, 0.930, and 1, corresponding, respectively, to butylbenzene weight fractions of 0, 0.0115, 0.25, 0.35, 0.50, 0.60, 0.75, 0.90, and 1. The corresponding parameters for the mixtures, and the mean and maximum deviations in volume, are obtained up to 40 and 100 MPa (in parentheses). The maximum mean deviation in volume for a given mixture is observed in pure butylbenzene as 1.20%, while the lowest

Table V. Characteristic Average Parameters for x_1 n -Butylbenzene + x_2 C_{10} + $(1-x_1-x_2)$ C_{14} Mixtures

x_1	0.578	0.561	0.552	0.544	0.529
x_2	0.109	0.212	0.261	0.308	0.399
$10^{-6}\langle v^* \rangle$ ($\text{m}^3 \cdot \text{mol}^{-1}$)	17.296	17.344	17.368	17.392	17.441
$\langle \varepsilon^* \rangle$ (K)	164.91	165.07	165.15	165.23	165.37
$10^{-3}\langle V^* \rangle$ ($\text{m}^3 \cdot \text{kg}^{-1}$)	1.1704	1.1731	1.1745	1.1759	1.1758
$\langle T^* \rangle$ (K)	10037	9873	9793	9714	9561
$\langle P^* \rangle$ (MPa)	807.9	806.9	806.4	805.9	804.8
ΔV_{mean} (%)	0.50 (0.55)	0.54 (0.58)	0.61 (0.61)	0.62 (0.65)	0.64 (0.72)
ΔV_{max} (%)	0.75 (0.79)	0.78 (0.78)	0.87 (0.87)	0.89 (0.89)	0.91 (1.01)

mean with 0.11% in volume is in pure *n*-tetradecane. The results for binary mixtures are virtually in agreement in the range. But as reasoned in the alkane mixtures, volumetric deviation decreases from butylbenzene to *n*-tetradecane.

In Table IV, *n*-heptane and nonylbenzene binary mixtures have been studied with the *n*-heptane weight fractions of 0, 0.05, 0.15, 0.25, 0.35, 0.50, 0.60, 0.75, and 1; their corresponding molar fractions are listed in Table IV. Using the corresponding parameters for the mixtures, the percentage mean deviation and maximum deviation in volume are observed in the range of 0.21 (0.31) to 0.88 (1.06) and 0.25 (0.32) to 1.34 (1.68) up to 40 MPa (100 MPa), respectively. The results are pretty well in agreement with the experiment.

In Table V, the ternary mixtures of butylbenzene, decane, and tetradecane are employed with weight fractions of 0.50 butylbenzene with 0.10, 0.20, 0.25, 0.30, and 0.40 decane. Their corresponding molar fractions are summarized in Table V with the average parameters and deviations in the theoretical volume from the experimental one. The observed percentage deviation in volume ranges from 0.50 (0.55) to 0.64 (0.72), and the maximum deviation observed is 0.92 (1.01) up to 40 MPa (100 MPa). Satisfactory agreement is apparently obtained for ternary mixtures.

5. CONCLUSION

The investigation of binary and ternary mixtures of hydrocarbons illustrated once more the quantitative performance of the SS theory for physical mixtures. Most importantly, it turns out to be possible to take the advantage of the decomposed parameters obtained for the group interaction parameters, i.e., the intersegmental pair potentials' minima ϵ_{ij}^* , and their locations' cubes v_{ij}^* . Consequently, reasonable predictions of *PVT* properties for alkane and alkane-alkylbenzene mixtures have been obtained for a broad range of temperature and pressure. This shows that the range of applicability of the group interaction parameters, tested successfully for pure alkanes and alkylbenzenes, can be extended to other hydrocarbons. If not yet available, new group parameters for different structural segments must be obtained for predictive purposes.

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